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New PAH mode at 16.4 μm ^{*}

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Abstract. The detection of a new 16.4 μm emission feature in the ISO-SWS spectra of NGC 7023, M17, and the Orion Bar is reported. Previous laboratory experiments measured a mode near this wavelength in spectra of PAHs (Polycyclic Aromatic Hydrocarbons), and so we suggest the new interstellar 16.4 μm feature could be assigned to low-frequency vibrations of PAHs. The best carrier candidates seem to be PAH molecules containing pentagonal rings.

Key words: Interstellar medium: molecules, extinction

1. Introduction

The launch of ISO (Infrared Space Observatory, Kessler et al. 1996) has vastly improved our ability to explore the spectral range beyond 13 μm , which is blocked by atmospheric absorption. Airborne or spaceborne mid-infrared spectrometers prior to ISO did not have the sensitivity to determine whether the carriers of the Aromatic Infrared Bands (AIBs), observed in the interstellar medium (ISM) between 3 and 13 μm , also emit at longer wavelengths.

The lack of interstellar data on possible AIBs at 13 – 25 μm meant that laboratory spectroscopy of interstellar analogs in this spectral range was scanty. The hypothesis that polycyclic aromatic hydrocarbons (PAHs) are responsible for the AIBs (Léger and Puget 1984, Allamandola et al. 1985), has led much laboratory work to focus on PAHs. Spectra longward of 13 μm were initially published for a limited sample of small PAH molecules (Léger et al. 1989a; Karcher et al. 1985; Allamandola et al. 1989). Recently a more extensive laboratory study (Moutou et al., 1996) has shown that PAH spectra contain common vibrational frequencies, namely near 16.2, 18.2, 21.3 and 23.2 μm (617,

550, 470 and 430 cm^{-1}). These frequencies where many species exhibit an absorption mode should correspond to modes with a higher probability of detection in the ISM. The IR spectra of many neutral and ionized PAHs isolated in Argon matrices have also been recently reported (Hudgins and Sandford 1998a,b,c).

Small particles such as PAHs in the ISM are believed to emit when they are heated to high temperatures by transient heating (Sellgren 1984), while laboratory absorption spectra are measured at lower temperature. This results in band broadenings and wavelength shifts of the interstellar emission features compared to the laboratory absorption features. The central wavelengths of PAH vibrational bands are observed to increase with temperature, and anharmonicity as well as mode couplings contribute to the broadening (Joblin et al. 1995). We have used the results of Joblin et al. (1995) to correct the measured central wavelengths of features under laboratory (absorption at lower temperature) conditions to the expected wavelengths under astronomical (emission at higher temperature) conditions.

In this paper, we compare the laboratory measurements of PAHs in the 14 – 25 μm domain to astronomical spectra obtained by ISO.

2. Observations

High-resolution Short Wavelength Spectrometer (SWS) spectra (de Graauw et al. 1996) of NGC 7023, M17, and the Orion Bar were obtained with ISO in a $14'' \times 27''$ beam. The data reduction was carried out with SWS-IA (update: October 1997). Bands 3A (12.0 – 16.5 μm) and 3C (16.5 – 19.5 μm) are subject to fringing (Schaeidt et al. 1996). Fringes were removed by subtracting a sine function, whose amplitude and phase were determined by least-squares fitting, from the high-frequency part of each detector scan. The order edge between bands 3A and 3C occurs at 16.5 μm , and is visible in Figure 1. A detailed description of the data reduction scheme is given in Moutou et al. (1999).

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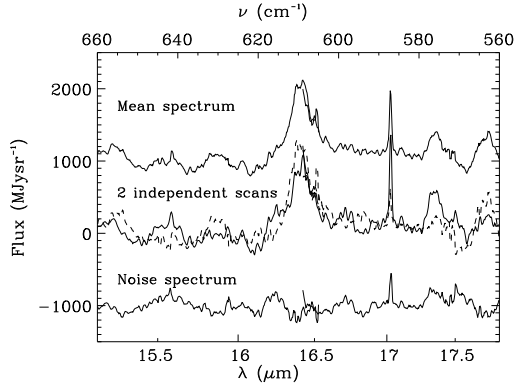


Fig. 1. ISO-SWS01 (dashed) and SWS06 (solid) spectra of NGC 7023 between 15.1 and 17.8 μm (660 – 560 cm^{-1}), at spectral resolution $R = \lambda/\Delta\lambda = 900$ and 1800, respectively. The two independent scans in the middle show the same emission feature at 16.4 μm , whereas noise features are not reproduced from one spectrum to the other (e.g. at 15.5, 17.4, and 17.6 μm). The 0–0 S(1) pure rotational line of H_2 is seen at 17.0 μm . The bottom plot, shifted by $-1000 \text{ MJy sr}^{-1}$ for clarity, is a noise spectrum obtained by subtracting one spectrum from the other after rebinning to $R = 900$. The upper spectrum is the average of both spectra, rebinned to $R = 900$, and shifted by $+1000 \text{ MJy sr}^{-1}$.

2.1. NGC 7023

We observed the bright reflection nebula NGC 7023 at a position $27'' \text{ W } 34'' \text{ N}$ of its illuminating star HD 200775. The SWS01 spectrum (2.5 – 45 μm) has a spectral resolution of $R = \lambda/\Delta\lambda = 900$ (Sellgren et al. in preparation). Another spectrum with SWS-AOT6, at $R = 1800$, provided an independent spectrum in the reduced domain 14.5 – 19.5 μm on which we focus here. The continuum level in this object is quite low and almost flat between 13 and 25 μm , which offers the best conditions for searching for new features. Comparison of spectra taken at different times is a reliable test for distinguishing noise features from real emission bands. Both spectra are displayed in Fig. 1. The SWS slit orientation differed between these spectra, which explains the varying intensity of the 17.0 μm H_2 line.

The spectra contain an emission feature at 16.4 μm , detected in all independent scans. This new emission feature was first mentioned by Boulanger et al. (1998) and Tielens et al. (1999). We have fit the 16.4 μm band in our SWS data by a Lorentzian profile (Fig. 2). Lorentzian fitting of AIB spectra has proven to be a useful tool for extracting the band contribution from the underlying continuum (Boulanger et al. 1998).

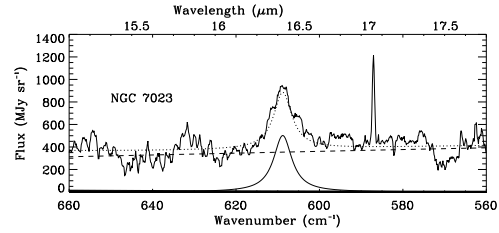


Fig. 2. Lorentzian fitting of the 16.4 μm band in the SWS01 spectrum of NGC 7023. The dashed line indicates the underlying continuum and the dotted line shows the sum of continuum and Lorentzian band. The H_2 line was not fitted.

Parameter	NGC 7023	M17-SW	Orion Bar
ν ¹	609.0	609.3	608.4
FWHM ²	6.6	5.3	5.6
I ³	1.15 (0.11)	1.07 (0.17)	2.65 (0.26)

Table 1. Observed parameters of the 16.4 μm band

¹ Band center in cm^{-1} ,

² Full width at half maximum in cm^{-1} ,

³ Integrated band intensity in $10^{-6} \text{ W m}^{-2} \text{ sr}^{-1}$. The 1σ uncertainty is given in parenthesis.

2.2. Detection in other objects

As shown in Fig. 3, the 16.4 μm band is also detected in the ISO-SWS01 ($R = 900$) spectra of the Orion Bar ($\alpha_{2000} = 5 : 35 : 20.3$, $\delta_{2000} = -5 : 25 : 20$), and in M17-SW, at the interface between the HII region and the molecular cloud ($\alpha_{2000} = 18 : 20 : 22.1$, $\delta_{2000} = -16 : 12 : 41.3$). More details on these spectra are given in Verstraete et al. (in preparation).

Individual values of the band parameters are listed in Table 1. The average central wavelength of the feature is 16.42 μm (608.9 cm^{-1}) and the average band width is 0.16 μm (5.8 cm^{-1}). The uncertainty in the intensity is based on the difference between independent scans and does not include the overall calibration uncertainty of SWS. Some variation in the band-to-continuum ratio at 16.4 μm is observed, likely due to the stronger radiation field in M17-SW and the Orion Bar. This will be discussed further in a forthcoming paper.

3. Laboratory spectra

The laboratory spectra of many PAHs contain a frequently observed mode peaking at 16.2 μm (Moutou et al. 1996; Schmidt et al., not published; Hudgins & Sandford 1998a,b,c). This mode appears slightly shifted from one molecule to the other, because its frequency depends on the internal structure of the molecular skeleton. In total, 29 molecules out of 63 show a band in between 611 and 623 cm^{-1} (16.21 – 16.52 μm).

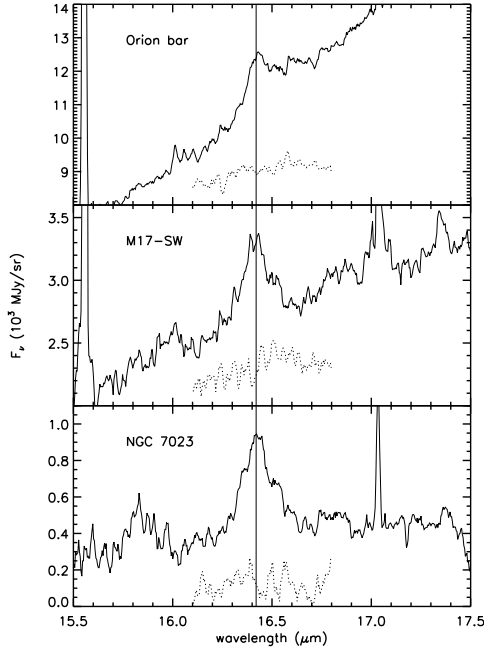


Fig. 3. The 16.4 μm feature in ISO-SWS01 spectra (solid lines) at $R = 900$ of the Orion Bar, M17-SW, and NGC 7023 (see text for positions). The dotted lines show the difference between independent upwards and downwards spectra, as a noise estimate. The strong line at 15.5 μm in Orion and M17 is [Ne III].

The central wavelength of a PAH vibrational mode should appear redshifted in interstellar spectra, with respect to the position measured in absorption at cooler temperatures (Joblin et al. 1995). The averaged redshift observed for coronene over ~ 300 Kelvins is approximately 1% of the vibration wavenumber. This would move the measured wavelength of the laboratory 16.2 μm band to the observed wavelength of the interstellar 16.4 μm band.

Fig. 4 shows the measured histograms of the laboratory absorption modes, obtained by counting the modes, in 5 cm^{-1} bins (or 0.13 μm bins). It has been done separately for the seven PAH families previously defined in the far-infrared data base of PAH spectra (Moutou et al. 1996). This number is a percentage, normalised to the total number of species in the corresponding family. Each family contains generally 5 to 9 individual species. The "PAHs with pentagons" family has 19 components and the "chain PAHs" contains 6 additional species taken from the work of Hudgins and Sandford (1998a,b), leading to a total number of 11 "chain" species. The 0.16 μm redshift is applied to the laboratory data. We deliberately did not take into account in this statistical approach the relative strength of the modes and it is thus not similar to a spectrum, because of the difficulty of combining spectra

from three different laboratory groups. However, the average spectrum of each PAH family measured by Moutou et al. 1996 is displayed in their Figure 1, and these average laboratory spectra can be directly compared to the interstellar spectra after applying a 0.16 μm redshift to the laboratory data.

We find that the 16.4 μm band is especially active in the spectra of PAHs containing pentagonal rings and of linear PAHs. In this latest category, the band appears more likely at 16.25 μm and is dominated by the spectra of small chains containing 2 to 5 rings. These molecules are not thought to be good candidates as IR emitters, as they will probably not survive the interstellar radiation fields (Omont, 1986). Comparatively, the distribution of modes for other kinds of PAHs in this spectral domain is more spread out in wavelength or has another accumulation point. The contribution of the PAHs containing pentagons could then possibly dominate the interstellar emission spectra we observe.

4. Discussion

Calculations of infrared spectra are rare for large molecules. In our sample of PAHs with pentagons, only the theoretical spectrum of fluoranthene ($\text{C}_{16}\text{H}_{10}$) has been calculated (Klaeboe et al. 1981). The mode is observed at 616 cm^{-1} in the laboratory and predicted by simulations to lie at 668 cm^{-1} ; it is identified as a B2 in-plane vibration of C–C bonds. It is a complex vibration of the global ring structure, which could be described as a tentative "rotation" of the central pentagonal ring (J. Brunvoll, private comm.) and consecutive movement of all carbon atoms. In other molecules, it may also correspond to a *global vibration of the carbon skeleton*. Since the mode is also present in PAHs without pentagons, it is not clear yet if the five-membered rings have a special role in the IR activity at 16.4 μm . We investigate in any case the implications of the presence of pentagonal rings in PAHs:

- Pentagonal rings inside a PAH molecule are known to produce a strong feature around 7 μm (Moutou et al. 1996, Hudgins & Sandford 1998c). No individual feature is detected at 7 μm in NGC 7023, but we can place an upper limit on any 7 μm band from pentagonal rings from the 7.0 μm continuum level (Moutou et al. 1999). We adopt the laboratory width of 0.14 μm for a pentagonal 7 μm band. We can then estimate an upper limit on the ratio of flux in the 7 μm band to flux in the 16.4 μm band of < 10 in NGC 7023. This upper limit on the flux ratio is not in conflict with the measured laboratory value (2.5).
- We conclude that the non-detection of a 7 μm feature would not rule out a possible signature of pentagons in the ISM at 16.4 μm .
- In laboratory spectra where a 16.2 μm mode is observed, other modes may be present, but at positions

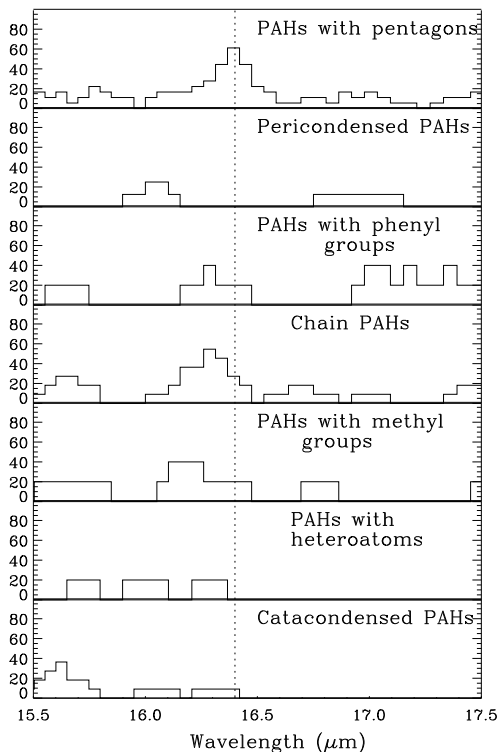


Fig. 4. Histograms of PAH modes measured in the laboratory (Moutou et al. 1996; Schmidt et al.; Hudgins & Sandford 1998a,b,c). They do not take into account the relative absorption cross sections. The modes are counted within bins with a 5 cm^{-1} ($0.13 \mu\text{m}$) width while the resolution element of the observed spectrum is 0.7 cm^{-1} . They are presented as a percentage in each family. The dashed line shows the position of the emission band in the ISO spectrum. A redshift of 6 cm^{-1} ($0.16 \mu\text{m}$) has been applied to all laboratory modes, in order to take into account the expected temperature effects ($\approx 300 \text{ K}$).

that vary a lot from one molecule to another (Moutou et al. 1996, and Fig. 4). These weak features are therefore under the detectability limit in our spectra.

- The fullerene molecule C_{60} , which contains pentagonal rings, and its related cation C_{60}^+ are not detected in NGC 7023 (Moutou et al. 1999). However, the C_{60} infrared spectrum does not show the $16.4 \mu\text{m}$ band (Krätschmer et al. 1990), for symmetry reasons. The low abundance of 60-atom fullerenes is therefore not evidence against pentagonal rings in the ISM.
- In the evolution of aromatic molecules, pentagonal rings tend to curve a molecular plane composed of pure hexagonal PAHs. The molecules will then become tri-dimensional while growing. A global scheme of aromatic compounds, from simple planar PAHs to small carbon grains or anthracite coals such as have been shown to fit the spectra of some planetary nebulae (Guillois et al. 1996) requires such an interme-

diate evolution state, where molecules of ~ 100 carbon atoms are curved. It is also consistent with proposals for grain formation in carbon star shells. For instance, Goeres & Seldmayr (1992), with their self-consistent model DRACON of carbon chemistry, predict the formation of large aromatic molecules containing pentagons, mostly from C_3 accretion, because pentagons offer the best trade-off between entropy and energy in the process of carbon dust growth. Also, Kroto & McKay (1988) proposed an alternative growth sequence to produce carbon grains, involving pentagonal rings. Their presence in the network would lead to “quasi-icosahedral carbon particles with spiral structures” (see also Balm & Kroto, 1990).

We have shown that the $16.4 \mu\text{m}$ mode observed in interstellar spectra could be explained by PAH vibrational activity. More work is required to assess the possible dominant role of five-membered ring PAHs. Other mid-infrared features should also be searched for in other ISO spectra, as the identification of other far-infrared features could give some important hints as to the nature of the AIB spectrum.

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